PRESSURE DISSOCIATION OF SOLID
NITROGEN UNDER 1 MBAR

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January 1985

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ABSTRACT

The zero-temperature transition pressure from molecular to monatomic nitrogen is predicted to be less than about 1 Mbar, and should be observable in diamond-anvil cells. This estimate is obtained from total energy calculations in which compressed molecular nitrogen is found to dissociate into a simple cubic monatomic structure, slight distortions of which are common to other Group V elements. The calculated 35% volume change raises the possibility of a large barrier to dissociation and extensive regions of metastability.

Recent shock wave experiments by Nellis et al.[1] show that fluid nitrogen undergoes a transition at modest pressures (300 kbar) and high temperatures (6000 K) that appears to be dissociation of the N_2 molecules to form a monatomic fluid. It is known that nitrogen remains in its molecular form in the solid at room temperature to pressures over 500 kbar,[2] so the observed transition is likely driven by the high temperatures. However, the relatively low transition pressure suggests that the monatomic state may be much more favorable than expected considering the strong N_2 molecular bond. If so, then nitrogen may have a diatomic to monatomic transition at pressures low enough to be seen in static experiments. The present paper reports calculations which support this possibility, and predict an extraordinary stability for the simple cubic (sc) structure of monatomic nitrogen. This puts nitrogen in line with other Group V elements where an arsenic-like A7 distortion of sc is common,[3] and the sc structure itself has been observed.[3a]

Calculations for five monatomic[4] nitrogen structures, sc, diamond, bcc, (ideal) hcp, and fcc, were carried out using the linear-muffin-tin-orbitals (LMTO) method, which is described in detail elsewhere.[5] The calculations were non-relativistic, used the von Barth and Hedin exchange-correlation potential,[6] and treated all electrons self consistently, with the outer five treated in a band mode. Brillouin zone sampling was sufficient to yield total energies accurate to within 0.0001 hartree/atom.

The one-electron potential was taken to be spherically symmetric within atom-centered spheres for the bcc, hcp, and fcc structures as is customary in LMTO calculations[5]; however, additional interstitial spheres were needed in the case of the more open sc and diamond structures. This, and inclusion of the Ewald (or muffin-tin) correction[7] to the electrostatic energy, are essential to get accurate energy differences between the open-packed sc or diamond structures and the more close-packed bcc, hcp, and fcc structures. Successful application and testing of this procedure for the structural energy differences in C and Si have already been reported.[8]

The total energies, relative to the $^4S_{3/2}$ ground state of the isolated N atom, for the five solid N structures are presented in Fig. 1 as a function of volume per atom. The isolated atom energy was taken to be -54.2557 hartree/atom, obtained by a spin-polarized calculation (with the von Barth–Hedin exchange-correlation potential) in which all three 2p electron spins were taken parallel. This procedure yields a cohesive energy of 0.11 hartree/atom for sc N at a zero-pressure volume of 41.4 bohr^3/atom. Use of the alternate Hedin–Lundqvist exchange-correlation potential[9] for both the monatomic solid and the isolated atom reduces the cohesive energy by 11%. Therefore we shift the N-phase energies upward by 0.01 hartree/atom in our following estimate of the uncertainties.

The structural properties and total energy of solid N_2 were obtained using a recently reported method[10-11] based on the Gordon-Kim electron-gas model[12] for calculating the short-range interactions between closed-shell atoms and molecules. This method yields results for the zero-temperature properties of a number of molecular solids in good agreement with experiment. For nitrogen, it gives the zero-pressure lattice constant and cohesive energy within 0.1 and 7% (or only 0.0002 hartree/molecule), respectively, of experiment.[11]

In these calculations the electronic distribution of the nitrogen molecule is assumed to remain unchanged from the gas-phase distribution, even in the high-pressure solid. A recent test of this approximation for solid Ar found that the changes induced in the electronic distributions of the Ar atoms by the high-pressure environment were reasonably small, lowering the calculated total free energy by only 0.006 hartree/atom at 750 kbar.[13] While solid N_2 is likely to experience a somewhat larger pressure effect, the change in bond length has been estimated[2] from Raman spectra to be only about 0.02 bohr at 374 kbar, and thus should not affect the energy greatly. This is consistent with solid I_2, where the I_2 bond length is known to remain constant to within 2% all the way up to 210 kbar where dissociation occurs.[14]

At low temperatures, the structure of solid N_2 above 20 kbar is thought to be of rhombohedral symmetry with eight molecules per primitive cell and space group $R\bar{3}c$.[15] Changes in the phonon spectrum

indicate a transition[15] at about 200 kbar, possibly to R3c. Since theoretical calculations exceeding 750 kbar continue to find the $R\bar{3}c$ structure to be the most stable among those considered (including R3c),[11a] we assume the $R\bar{3}c$ structure for all N_2 calculations. Note that in the volume regime considered below for the dissociation of the N_2 lattice, the N-N separation between molecules is more than twice the N_2 bond length, and differences in energy between plausible structures for the molecular phase are small compared to the scale of the N to N_2 differences. We subtract the molecular dissociation energy ($D_e = 0.3640$ hartree/molecule)[16] from the molecular total energies (calculated relative to the $^1\Sigma_g^+$ ground state of the free molecule), and divide by two to obtain the N_2 results in Fig. 1 relative to the $^4S_{3/2}$ atomic ground state.

The two curves for N_2 in Fig. 1 correspond to different choices of a parameter in a function used to damp the dispersion energy at small separations.[11b] The curve at larger volumes used a value chosen to yield good agreement with the low-pressure phase diagram, but the resulting pressure-volume curve at 100 kbar was slightly too stiff. We chose[11a] a value for the set of calculations at smaller volumes which gave agreement with the experimental volume[17] at 100 kbar. While the latter curve was used below in our estimates of the dissociation pressure, the energies obtained from these two sets of N_2 calculations do not differ greatly. An earlier calculation, with a different

description of the dispersion energies, gave results almost identical with the curve at small volumes.[10b] With these and the above-mentioned uncertainties, we estimate the error in the molecular curves to be roughly 0.01 hartree/molecule.

A common tangent construction between the molecular and monatomic curves in Fig. 1 indicates a zero-temperature transition from solid N_2 to a sc phase of N at about 770 kbar. Previously mentioned uncertainties for both N and N_2-phase energies, as well as an estimate of the zero-point energy difference between phases,[18] could raise this pressure to about 940 kbar. The volume change for the transition is quite large, about 35%. A transition to the diamond structure would take place at about 2 Mbar with a volume change of about 17% and to the fcc structure at about 3 Mbar with a 16% volume change.

Some insight into the stability of a sc (or distorted sc) N phase is gained by considering calculations on the Group IV elements.[8,19] Diamond phase N has a large gap between bonding and antibonding hybrid-sp^3 levels which is comparable to that of C. However, the additional valence electron possessed by N must go above this gap, destroying the highly favored status of the diamond structure. In contrast, the sc structure has only a dip in the density of states near the Fermi level, which is sufficiently broad to favor this phase over such structures as bcc and fcc; regardless of whether there are four (C) or five (N) valence electrons. The A7 distortion of sc apparently deepens this dip

at the five-electron Fermi level to the point of semimetallic behavior by providing greater separation between bonding and antibonding p[3] levels, with both bonding and antibonding s levels being occupied.[20] In P and As the resultant lowering of the band structure energy is gradually surpassed under pressure by the lower electrostatic Madelung energy of the more symmetric sc phase,[21] so that the A7 structure is observed[3] to deform towards sc under pressure.

While it is likely that nitrogen, like phosphorous, will eventually reach the sc structure, phases not considered here may well intervene. Thus our calculations suggest an upper bound to the transition pressure. The three-fold coordinated, rhombohedral A7 structure is one obvious candidate for an intermediate phase. We attempted LMTO calculations for this structure, and did obtain lower energies than sc. Unfortunately, increasing distortion away from sc brings the A7 structure, even with interstitial spheres, rapidly into a region of low packing fraction and low symmetry where the LMTO method as used here becomes unreliable.[8] The even lower symmetry, three-fold coordinated, orthorhombic, black-phosphorous structure[22] is another possibility. With weak van der Waals interactions between sets of strongly bonded double layers,[22] such a phase might well permit destruction of the diatomic bond in nitrogen without requiring the immense volume change seen here.

In summary, our calculations suggest that solid N_2 will undergo dissociation to a monatomic lattice below 1 Mbar, which is within the reach of static high-pressure experiments. We also predict, for the first time, that nitrogen will behave like other Group V elements in showing a tendency to assume the sc structure under pressure. Intervening phases may well result in dissociation at lower pressures with a far smaller volume change than the 35% seen here; however, the possibility of a large volume change cannot be ruled out. Indeed, a transition from the N_2 molecular phase (each atom triply bonded to its sole near neighbor) to either of the A7 distorted sc or the black-phosphorous structures (each atom singly bonded to three near neighbors) is suggestive of a polymerization transition where large volume changes are not uncommon. Furthermore, there may be a large barrier to dissociation due to the energy necessary to break the strong triple bond in the N_2 molecule, raising intriguing kinematic questions, and the possibility of considerable hysteresis in actually making the dissociated phase. The reverse argument suggests a low-pressure region of metastable monatomic phase, which would make monatomic nitrogen an exceedingly interesting material.

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18. We estimate the zero-point energy E_{zp} of sc N to be 0.0048 hartree/atom at zero pressure, based on $E_{zp} = \frac{9}{8}\hbar\omega_D$ and $\omega_D \sim$

$k_D(B/\rho)^{1/2}$, where k_D is the Debye wavevector, B is the bulk modulus, and ρ is the density. The volume dependence is found assuming a Grüneisen parameter of 2. For the N_2 phase we take the sum of the intramolecular E_{zp} (0.00536 hartree/molecule, Ref. (16) and the intermolecular E_{zp} of the solid (e.g., 0.00626 hartree/molecule at zero pressure), which is estimated using Eq.(8) of J. C. Raich and R. L Mills, J. Chem Phys. **55**, 1811 (1971).

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FIGURE CAPTIONS

Fig. 1 Total energy versus volume for various phases of solid diatomic ($R\bar{3}c$ structure, labeled N_2) and monatomic (labeled N) nitrogen at T=0. The structures corresponding to the monatomic curves are: simple cubic (lower dotted curve); diamond (chain-dotted); bcc (dashed); hcp (chain-dashed); and fcc (upper dotted curve). The two solid curves for N_2 differ in treatment of the dispersion energy, as described in the text.